

# **Temporal and Spatial Scales of Terrestrially-derived Particulate and Dissolved Materials in the Penobscot River System: Quantifying Conserved and Non-conserved Optical Properties and Transformations within the Estuary**

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## **LONG-TERM GOALS**

Coastal waters represent the commingling of offshore marine and terrestrial surface source waters and therefore are naturally complex and variable. Our long term goal is to establish observational and modeling approaches to predict sources and scales of variability in the source waters, particularly those related to land use activities in upstream watersheds, from observations and measurements in the coastal waters.

## **OBJECTIVES**

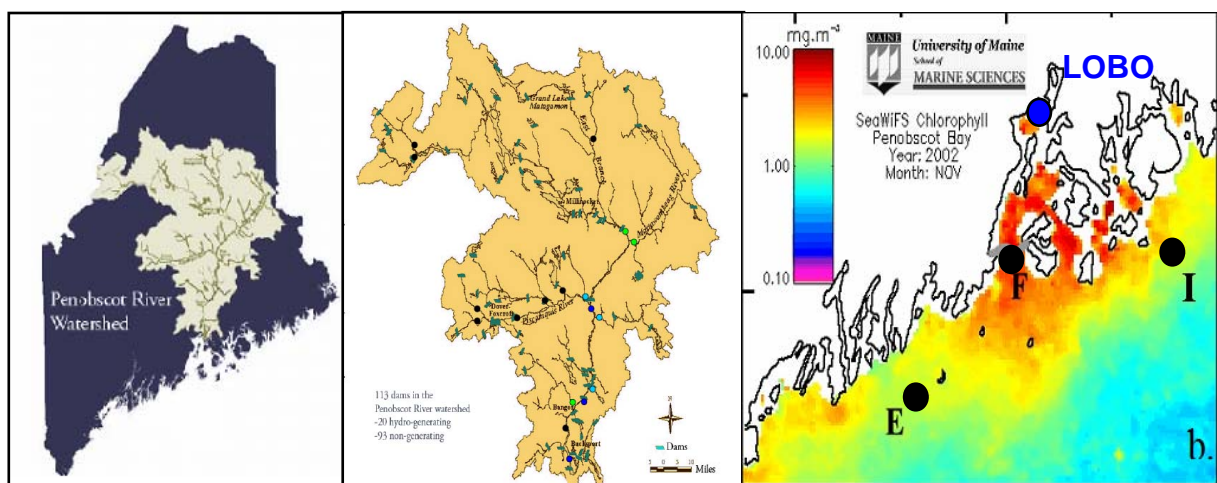
Hydrologic optics provides an approach to characterizing physical and biogeochemical processes in aquatic systems over a range of time and space scales. The linkage between observations of the inherent optical properties (IOPs; absorption, scattering and fluorescence) and the geophysical properties lie in the establishment of robust optical proxies and the quantification of the temporal and spatial scales over which these proxies remain conservative in their properties. Our objectives are to identify and quantify specific optical and chemical characteristics of the colored particulate and dissolved fractions originating in the Penobscot River system that are associated with defined land use activities (land use proxies), and to determine the scales of variability over which these proxies can be detected both temporally (i.e. seasonal and episodic events) and spatially (from the source into coastal waters).

## **APPROACH**

Our approach combines high resolution temporal and spatial hydrographic and optical observations from moored, surface underway and undulating platforms with chemical characterization of the organic and inorganic, particulate and dissolved carbon and nitrogen pools that originate in the sub-watershed drainage basins of the Penobscot River System and flow through Penobscot Bay estuary into the coastal waters of the Gulf of Maine. Our approach is to (1) identify optical proxies for biogeochemical parameters, including quantifying the time and space scales of conservative behavior;

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(2) apply these proxies to high-resolution time and space optical observations to compute concentration and flux of river borne material into the estuary and coastal systems; (3) compare models for conserved behavior with observations to identify zones and times of non-conserved behavior; (4) elucidate transformation processes at these locations/times; (5) quantify impacts of land use on the biogeochemical properties of the coastal ocean with the goal to predict responses to climate induced hydrologic forcing.



**Figure 1. Sampling Program for Penobscot Watershed and coastal waters. A. Map of the state of Maine with the Penobscot River and Watershed indicated. B. Detail of Watershed showing location of monthly sampling stations (green) and moored triplet sensors (blue). C. SeaWiFS false color image of November chlorophyll concentration showing high values of apparent chlorophyll induced by high CDOM flowing out of the Penobscot River and Bay and into the waters of the Eastern Maine Coastal Current. The locations of Penobscot LOBO (blue) and GoMOOS Buoys E, F and I (black) indicated by circles.**

## WORK COMPLETED

Observation Programs (Figure 1), Sample Processing and Data Analysis

1. Monthly Watershed Samples- We have completed 48 monthly sampling trips of the subtributaries of the Penobscot River as of December 2008. Samples are processed for particulate and dissolved optical, carbon and nitrogen properties, and in situ discrete optical properties (e.g. backscattering and CDOM and chlorophyll fluorescence), temperature, conductivity, pH and dissolved oxygen. *This observational data set is used for analysis of river flux and development of optical proxies.*
2. In situ Triplet Deployments- We have deployed WETLabs triplet sensors (e.g. backscattering and CDOM and chlorophyll fluorescence) at 1-3 locations in the lower Penobscot River to capture high resolution observations associated with different flow regimes and seasons. These observations are converted to biogeochemical observations via the optical proxies. *These observations provide the basis for the high temporal resolution freshwater endmember biogeochemical/optical dynamics.*
3. Penobscot Bay Field Surveys- Working with A. Barnard, we have participated on a total of nine survey programs in Penobscot Bay to elucidate the transformation processes of dissolved and

particulate matter originating from the river and transported to the coastal waters. *These observations provide the high spatial resolution biogeochemical/optical estuarine process dynamics.*

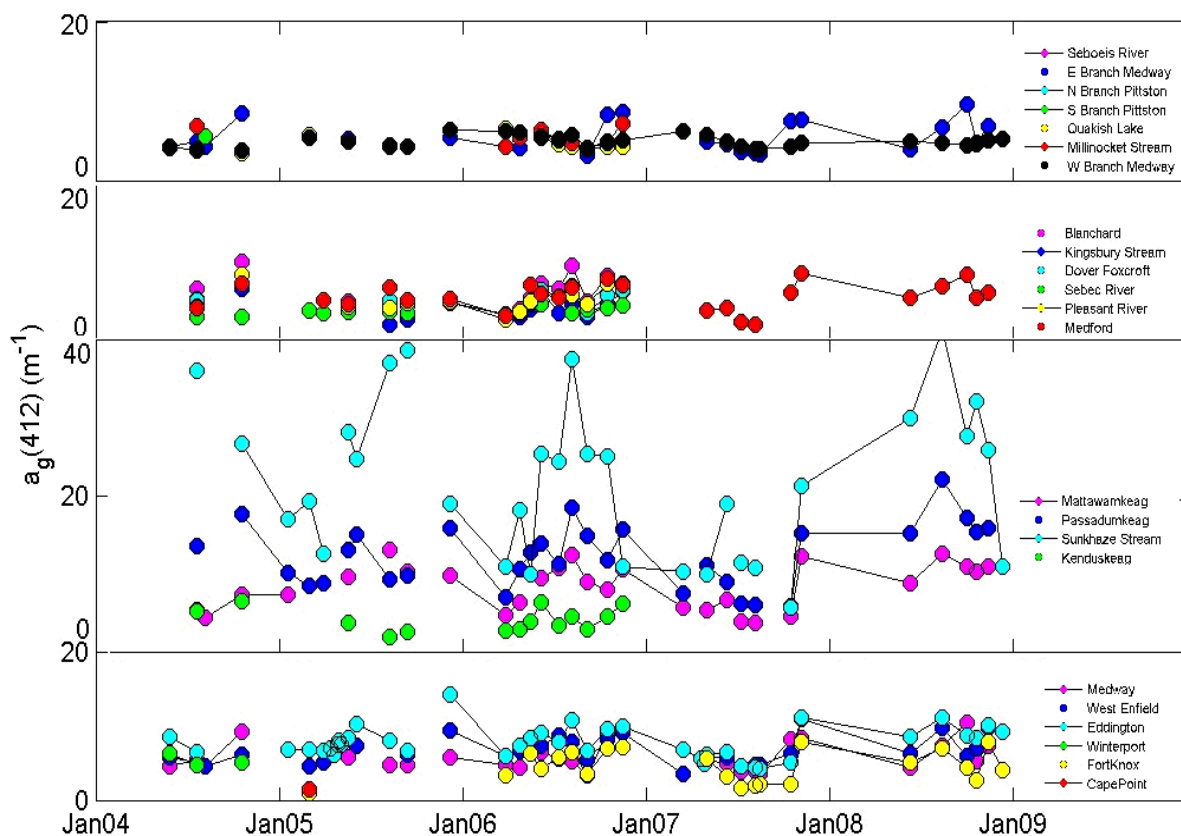
4. LOBO observations in Penobscot Bay – We are currently in the second year of deployment of the LOBO realtime observational system ([www.loboviz.com/penobscot](http://www.loboviz.com/penobscot)). In addition to the standard water quality measurements, we have deployed a LISST 100 particle size analyzer to elucidate the particle dynamics simultaneous to the CDOM dynamics at the location previously identified as the zone of non-conservative CDOM behavior. *These observations provide the basis for determining if and how organic matter is transformed between particulate and dissolved phases and how that leads to the non-conservative processes in the estuary.*

5. GoMOOS Buoy Optical Observations- We continue to deploy and maintain optical sensors on the GoMOOS platforms with funding from this project (the GoMOOS funding ended in early 2007). These include ocean color sensors (e.g. multispectral downwelling irradiance and upward radiance), CDOM and chlorophyll fluorometers and backscattering sensors on buoys F, E and I, as well as ac9 observations on E and I. Water samples are collected during the deployment/recovery cruises twice per year for biogeochemical analyses. *These observations provide the basis for the high temporal resolution marine endmember biogeochemical/optical dynamics.*

## **RESULTS**

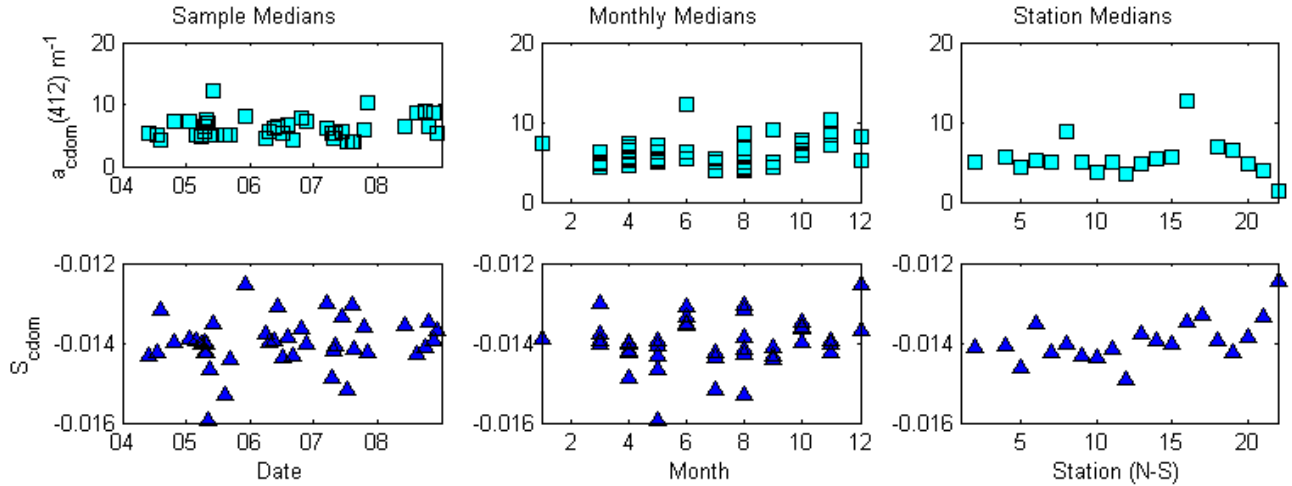
### **RIVER BORNE OPTICAL CONSTITUENTS**

Riverine transport of particulate and dissolved material demonstrates variable temporal and spatial patterns in the constituent optical properties (e.g. CDOM, Figure 2). Strong interannual variations are observed, particularly dependent upon precipitation and discharge events. Statistical analysis of the patterns of variability reveal interannual, monthly and location-dependent variability (Figure 3, left, center and right panels, respectively).



**Figure 2. Example of time series of discrete optical observations collected in the watershed 2004-2008. Shown is the absorption coefficient at 412 nm for the colored dissolved organic matter ( $m^{-1}$ ).**

**Value range from order 1 to order 40  $m^{-1}$  depending upon season and tributary. Top panel: Northern subwatersheds associated with forested and lumbered land cover/use. Second panel: Piscataquis River subwatersheds associated with agricultural land use. Third panel: Subwatersheds dominated by freshwater bogs; the CDOM absorption coefficients are maximal in these tributaries and maximal values occur during high precipitation periods. Bottom panel: Maine Branch Penobscot River stations showing the cumulative effect of each tributary contribution to CDOM absorption. Lowest values observed at stations impacted by seawater from Penobscot Bay, highest values at lowest freshwater station (Eddington).**

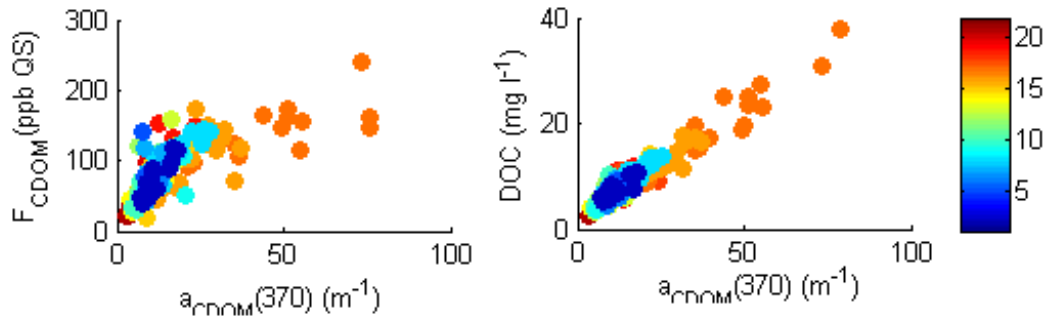


**Figure 3. Statistical analysis of CDOM absorption measured over the four year time series. Top panel: the magnitude of the CDOM absorption coefficient at 412 nm ( $m^{-1}$ ) shown in Figure 2.**

**Bottom panel: the spectral slope of the CDOM absorption coefficient,  $S_{CDOM}$ . Interannual variability is shown in the left panels, 2005 and 2007 had statistically higher coefficient and greater slope variations than other years. Monthly median observations shown for each station are shown in center panels. April, August and November has statistically the highest CDOM absorption, and generally steepest spectral slopes. Station-specific variations are shown in the right panels. Stations associated with wetlands exhibited the highest CDOM absorption. Stations seawater-impacted exhibited flattest spectral slopes.**

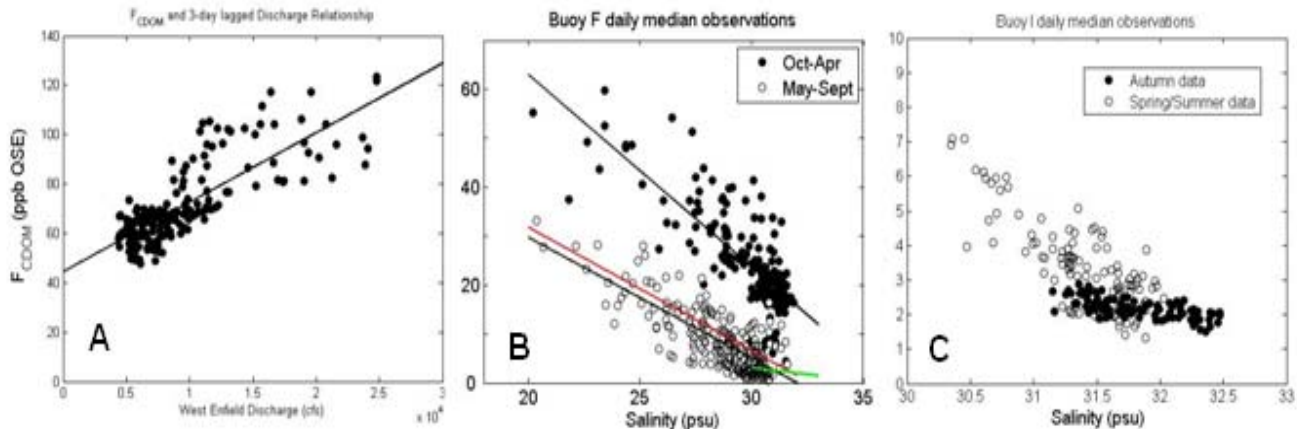
## OPTICAL PROXIES

Watershed Optical Proxies for Biogeochemical Parameters are quantified from paired optical observations and biogeochemical analyses collected on monthly watershed sampling trips, semi-annual estuary surveys and occasional buoy operations trips. An example of the optical proxy relationships are shown in Figure 4 for dissolved matter. The in situ CDOM fluorometer is significantly related to the CDOM absorption coefficient at the excitation wavelength. The largest variations in the fluorescence to absorption relationship is found at wetland stations where the fluorescence quantum yield is much lower than for other samples. Dissolved organic carbon (DOC) for this river is strongly related to optical proxies, for example, the absorption coefficient, regardless of season or station (Figure 4).



**Figure 4. Example of optical proxies for dissolved fraction. Left panel shows the relationship between in situ CDOM fluorescence versus the CDOM absorption coefficient at the excitation wavelength (370 nm). A statistically significant relationship is observed with largest variability accounted for by wetland dominated tributaries. Right panel shows the very strong optical proxy ( $a_{CDOM}$ ) for biogeochemical parameter (DOC), with very little variability and no dependence on season or station.**

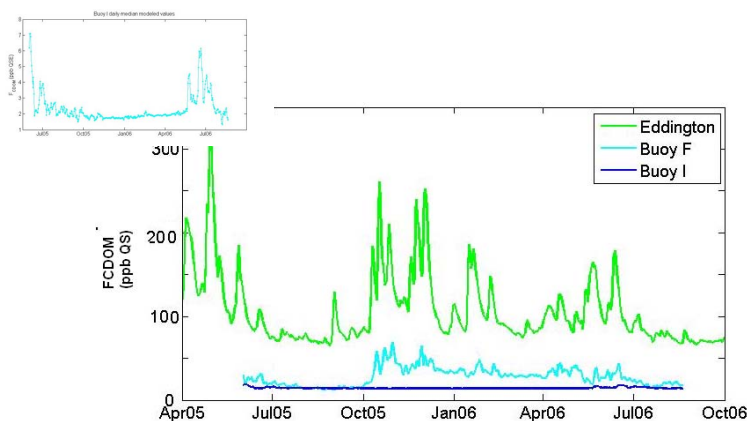
High temporal resolution of optical proxies for biogeochemical parameters are obtained via moored optical sensors within the Penobscot River to quantify export from the terrestrial environment (e.g. triplet/BBFL2 sensors), and in the Penobscot Bay estuary (e.g. Penobscot LOBO and GoMOOS buoy F) as well as in the coastal waters upstream and downstream of Penobscot Bay (e.g. GoMOOS buoys E and I). Our goal is to be able to quantify the source and variability of optical constituents in Penobscot Bay and in the downstream coastal waters. As an example, we have found that the concentration of dissolved matter (i.e. the magnitude of the fluorescence, absorption, and/or DOC) the lower Penobscot River is linearly related to the daily discharge (Figure 5A) and thus the source of CDOM entering Penobscot Bay can be reliably predicted from USGS daily discharge. In lower Penobscot Bay and the coastal waters upstream of Penobscot Bay, we have found that salinity provides a robust proxy for CDOM, although the relationship does have some seasonality to it (Figure 5BC).



**Figure 5. Conservative behavior of CDOM in the Penobscot system. A. Linear relationship between CDOM (fluorescence) and daily discharge, B and C. Linear relationships between CDOM fluorescence and salinity measured in lower Penobscot Bay (B- GoMOOS Buoy F) and in the coastal waters upstream of Penobscot Bay (C- GoMOOS Buoy I). The data cluster seasonally at both buoys. In (B) black lines indicate best fit regression for two data clusters. Red and green lines are regressions observed for the Buoy I (C) spring/summer and autumn data clusters, respectively. The spring/summer relationships are not statistically different for the two buoys.**

## MODELING CONSERVATIVE/NON-CONSERVATIVE VARIABILITY

Modeling conserved and non-conserved behavior of river borne material, e.g. CDOM, into the estuary and coastal waters starts with the pattern of export from the river. By combining the optical proxies derived from discrete observations, moored observations within the river and daily USGS discharge data, a 4-½ year time series of exported matter has been computed.

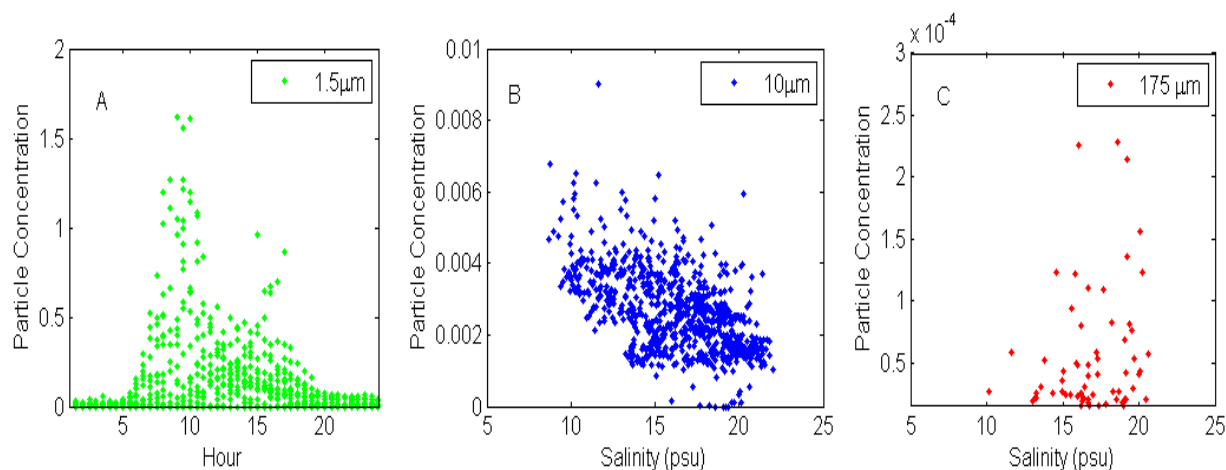


**Figure 6. Time series of CDOM fluorescence for freshwater source at Eddington (green), marine source (Buoy I, dark blue and cyan inset), and mixed water in Penobscot Bay (Buoy F cyan).**

Conservative mixing modeling demonstrates that the CDOM observed in lower Penobscot Bay is dominated by the source material entering via Penobscot River from October to April during the strong discharge period (with approximately 5 day lag from Eddington to Buoy F). However, in the spring and summer, the CDOM in lower Penobscot Bay is determined by the incoming CDOM from upstream coastal waters at Buoy I (it takes approximately 18 days to reach F from I). Contrary to expectation, it is during the high discharge, high CDOM concentration, high CDOM flux periods when the majority of CDOM is lost between Eddington and Buoy F (of order 40%) while during the low concentration, low discharge, low flux periods, upwards 90% of the CDOM is conserved.

## DISSOLVED PARTICLE TRANSFORMATIONS

Particle size distributions obtained from in situ deployment of the LISST at the LOBO site indicate that there is a very strong dependence of the particle field on tidal mixing. Three modes were observed in the particle size distribution. The two smallest size intervals detected by the LISST (particles between 1 and 2  $\mu\text{m}$ ) displayed no dependence upon tidal phase. Instead they exhibited the strongest dependence upon time of day, with the peak in particles observed at approximately 10 am and 3 pm local time. Particles of this size range were virtually absent from dusk to dawn (Figure 7A). This dynamic is suggestive of migrating zooplankton such as mysids, which is stunning given the extremely strong tidal velocities at this site. Particles of size range 2 to 50  $\mu\text{m}$  are inversely related to salinity, indicating a freshwater source. Lagged correlation analysis of the size intervals indicates that the 5 mm particles have the strongest correlation but that all particles in this range exhibit this dependence (Figure 7B). Conversely, particles exceeding 65  $\mu\text{m}$  exhibit the opposite dependence. When they occur, they only occur in conjunction with high tide conditions (regardless of salinity for that particularly tide); they are never observed during low tide conditions (Figure 7C). Interestingly there is no transition such that intermediate sized particles would be predominantly found during intermediate tide conditions. Thus for this month long deployment in June 2008, it appears that there is little transformation in the particulate phase or between the dissolved and particulate phase. Rather there is conservation of the high CDOM, high concentration of small particle waters entering Penobscot Bay from the River. We are in the process of examining the autumn deployments when we have observed CDOM loss between Eddington and Buoy F.



**Figure 7.** Analysis of particles of difference size classes as measured at the LOBO site with the Sequoia LISST for June 22 – July 12, observations collected every 30 minutes. **A.** Particles of diameter 1.5 mm exhibit the strongest variability as a function of time of day with peaks at 10 am and 3pm and virtual absence from dusk to dawn local time. **B.** Particles of size range 2-50  $\mu$ m (10  $\mu$ m shown here) exhibit an inverse relationship with salinity; **C.** Particles exceeding 65  $\mu$ m (175  $\mu$ m diameter particles shown here) display strong pulses of high concentration only at high tide. All correlations were significant. Lag correlation analysis was used to identify correlation with tidal phase.

## IMPACT/APPLICATIONS

It is apparent that the impact of the Penobscot River on coastal waters is significant from the perspective of both biogeochemistry and optics. What is encouraging is that optical proxies appear to be robust to estimate the important biogeochemical parameters including the concentrations of phytoplankton, non-algal particles, CDOM and their associated carbon concentration. Additionally, optical proxies for compositional characteristics are also robust. Finally, the export of materials can be modeled from easily monitored optical, hydrological and hydrographic properties. This suggests that forecasting is also probable. We have begun to correlate certain components with land use in the sub-basins, which can be traced out of the river and estuary and into the coastal waters. This suggests that offshore monitoring might be sufficient to identify terrestrial land use changes. We have begun the investigation into the particulate to dissolved phase transformations. We conclude that in the summer, when CDOM appears to be conserved, there is no transformation between particles and CDOM, consistent with modeling.

## RELATED PROJECTS

Both C. Roesler and A. Barnard are Co-PIs on a NASA sponsored multi-investigator research project examining the variability in fluxes of dissolved and particulate organic carbon from terrestrial sources to the Gulf of Maine via major rivers, and their subsequent fate within the Gulf of Maine. This work is specifically focusing on the impacts of riverine dissolved and particulate loading to the carbon cycle of coastal and offshore systems. Our ONR project is highly complementary to this project, as it is providing a better understanding of the variability in the concentration and composition of the

Penobscot River dissolved and particulate materials and its subsequent delivery to the coastal and offshore regions, with the emphasis on optical properties rather than carbon properties.

The Gulf of Maine Ocean Observing System (GoMOOS; data to be found at <http://gyre.umeoce.maine.edu/buoyhome.php>), which Dr. Roesler is funded by to maintain optical instrumentation and data streams from the mooring observation program, is providing valuable hourly time series of coastal optical and physical surface properties upstream and downstream of the Penobscot River. Beginning in the fall of 2004, optical sensors (backscattering, chlorophyll and CDOM fluorometers) were installed on a GoMOOS mooring in the center of the mouth of the western branch of Penobscot Bay. Data from these systems are providing a wealth of information as to the hourly to seasonal variability in the dissolved and particulate materials within the river to coastal transition zone of the Penobscot Bay. Additionally, CDOM fluorometers were added to the complement of sensors (ac9s, vsf, Ed and Lu) existing on the coastal shelf moorings upstream and downstream of Penobscot Bay. (include web links as appropriate/available).

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